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13. ABSTRACT (Maximum 200 words)  Studies in an ambient temperature chloroaluminate molten salt composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride were carried out. A variety of topics were investigated. The behavior of electroactive polymers, mainly polyaniline, was investigated, and simultaneous EPR and electrochemical experiments were carried out. The stoichiometry of several inorganic complexes ions was investigated in a near "neutral" melt, and a procedure to buffer the neutral melts was examined. A number of electrochemical studies with emphasis on the use of fast pulse voltammetry at very small microelectrodes were carried out. Finally, the chemistry and electrochemistry of solutes as influenced by the presence of a proton (Bronsted) acid were investigated by means of electrochemical and NMR techniques. Gutmann donor/acceptor numbers of the melts were obtained, and the behavior of dimethylaniline in the presence and absence of a Bronsted acid was examined. The presence of both Lewis and Bronsted adducts was confirmed.			
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**This is a Final Report on AFOSR 90-0099, Studies in Lewis Acid and Superacid Ionic Liquids.**

The research carried out under this grant involved studies of the chemistry and electrochemistry of ambient temperature chloroaluminate ionic liquids. The ionic liquids consist of mixtures of an organic chloride, 1-methyl-3-ethylimidazolium chloride, with aluminum chloride. A Bronsted acid was added in some instances and the resultant chemistry of solutes examined.

This activity was funded under a three-year option grant as of December 1, 1989, and expired June 30, 1992. Funding levels were \$120,325 (FY 1990), \$150,777 (FY 1991), and \$36,491 (FY 1992). The latter funding was for a seven month interval.

This Final Report discusses topics as submitted in our proposal in this area. In the interest of brevity, abstracts or summaries of work published will be used. All publications under this, and prior, AFOSR support are listed in Appendix A, as are listings of formal meeting presentations under the current grant.

The principal investigator left the State University of New York at Buffalo for North Carolina State University in July, 1992. The work reported below, with the exception of that in progress, represents work carried out at Buffalo.

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SUMMARY OF WORK: 1 DECEMBER, 1989 - 30 JUNE, 1992.

## **I. COMPLETED WORK**

### **A. Studies of Modified Electrodes in Ambient Temperature Molten Salts**

This continued work on the behavior of electroactive polymers in the molten salt system.

#### **1. Anthraquinone Containing Polymer**

A manuscript, "Electrochemistry of 9,10-Anthraquinone Moiety of [1-(Pyrrol-1-yl)-Hex-6-yl]-9,10-Anthraquinone-2-Sulfonate in Aluminum Chloride - 1-Methyl-3-Ethylimidazolium Chloride Ambient Temperature Melt" was published in the Journal of the Bangladesh Chemical Society; Bangladesh was the home of the post-doc involved in the work. See Ref. 106 in Appendix A.

### **ABSTRACT**

[1-(Pyrrol-1-yl)-Hex 6-yl]-9,10-Anthraquinone-2-Sulfonate has been synthesized and the compound analyzed by FT-NMR. The electroactivity of the anthraquinone moiety was investigated in the basic and acidic aluminum chloride - 1-methyl-3-ethylimidazolium chloride molten solvent and is found to be strongly influenced by the Lewis acidity of the melt. The compound has been polymerized at an electrode surface in the neutral melt. The polymer coated electrode was studied by cyclic voltammetry in the neutral and basic melts but did not show any electroactivity of the anthraquinone unit. The dissociation of the unit from the polymer or the failure of the large  $Im^+$  cation in the melt to diffuse through the polymer to permit charge neutralization on the reduced anthraquinone is suggested as the probable reason for the absence of electroactivity.

#### **2. Electrochemistry of Polyaniline**

Three manuscripts on this topic were published, two in Synthetic Metals, "Electrochemistry of Polyaniline in Ambient Temperature Molten Salts" and "Formation and Electrochemistry of Polyaniline in Ambient Temperature Molten Salts" and one in the Journal of Physical Chemistry, "Formation and Electrochemistry of Polyaniline in Ambient Temperature Molten Salts". See Ref. 110, 111 and 114 in Appendix A.

### **ABSTRACT**

Polyaniline (PAn) films obtained from acidic aqueous solution can be reversibly transferred between aqueous solution and an ambient temperature

molten salt consisting of mixtures of aluminum chloride with 1-methyl-3-ethyl-imidazolium chloride. The films show electrochemical activity in basic, neutral and acidic melts. The doping processes and deterioration mechanism are discussed for these melts. The redox reaction of Pan in basic melt is more stable and facile than in the other melts. The oxidized film is conducting and is insulating on reduction.

### ABSTRACT

Polyaniline (PAn) can be prepared on platinum and glassy carbon electrodes by anodic oxidation of the monomer in ambient temperature molten salts consisting of mixtures of aluminum chloride with 1-methyl-3-ethyl-imidazolium chloride. The formation and electrochemistry of PAn vary as the melt's composition is changed from 0.8:1 (basic) to 2:1 (acidic). The oxidation mechanism of aniline in melts differs from that in acidic aqueous solution and protons are not involved in the polymerization process. The peak potentials of PAn films in aniline-free melts shift to more positive potentials with increasing melt acidity. Transfer of PAn films between different melts and aqueous solution are reversible. Comparison of PAn cyclic voltammograms in aqueous solution with that in the melt suggests that cross linking and multiple substitution of the benzene ring probably take place during the propagation process and deterioration in aniline-free melts.

### ABSTRACT

Simultaneous EPR and electrochemical measurements have been carried out on polyaniline (PAn) prepared by monomer oxidation in an acidic aqueous solution and investigated in an ambient temperature ionic liquid, which consists of a mixture of aluminum chloride and 1-methyl-3-ethyl-imidazolium chloride. The maximum EPR response was found at the point where half the total observed charge had been passed in both cyclic voltammetry and potential step experiments. A one-to-one relationship between the number of spins observed and the number of electrons removed was found to about 25% of full oxidation. Experiments are explained in terms of two unresolved one-electron steps with a thermodynamic comproportionation equilibrium among the neutral, polaron, and bipolaron states. The equilibrium constant  $K_{\text{com}}$  of the reduced form,  $\alpha$ , and the oxidized form,  $\beta$ , changes with the conductivity and ionic environment of the film. The bipolaron is favored in the initial doping process, and the polaron is dominant in the final doping stage. The EPR response of the polaron decays with a half-life between 8 and 17 s.

### B. Studies in Neutral Melts

We attempted to examine some characteristics of the neutral molten salt system.

## 1. Stoichiometry of Complex Ions

A manuscript on this topic entitled "Determination of the Stoichiometry of Some Metal Chlorocomplex Ions in Basic Ambient Temperature Molten Salts" was published in the Journal of Electroanalytical and Interfacial Electrochemistry. See Ref. 102 in Appendix A.

### ABSTRACT

Oxidation waves of chloride at platinum microdisk electrodes in ambient temperature ionic liquid mixtures of 1-methyl-3-ethyl-imidazolium chloride and aluminum chloride were examined by normal pulse voltammetry to obtain information about the stoichiometry of several metal chlorocomplexes. It was found that  $\text{FeCl}_4^-$ ,  $\text{GaCl}_4^-$ ,  $\text{CdCl}_4^{2-}$ , and  $\text{SmCl}_6^{3-}$  are the only species present in basic melts, those containing excess  $\text{ImCl}$ . In solutions of  $\text{Nd(III)}$ , and equilibrium between  $\text{NdCl}_6^{3-}$ ,  $\text{NdCl}_5^{2-}$ , and  $\text{Cl}^-$  exists, for which the dissociation constant is evaluated as  $3.7 \text{ mol/m}^3$ . An ill defined wave that could be the oxidation of chloride from  $\text{CdCl}_4^{2-}$ ,  $\text{NdCl}_6^{3-}$ , and  $\text{SmCl}_6^{3-}$  is also observed. The Stokes-Einstein coefficient for chloride, using  $n=1$ , was found to be:  $D\eta/T = 2.53 \times 10^{-15} \text{ kg m/s}^2 \text{ K}$ .

## 2. Buffered Neutral Melt

A manuscript on a procedure to prepare a buffered neutral melt, and testing the system, was published in Journal of Electroanalytical and Interfacial Chemistry. See Ref. 105 in Appendix A.

### ABSTRACT

Mixtures of  $\text{AlCl}_3$  and 1-methyl-3-ethyl-imidazolium chloride form ionic liquids at ambient temperatures. It is shown that they may be buffered around their neutral composition point by metal chlorides.  $\text{Fe(III)}$  electrochemistry studied in a neutral melt buffered by the  $\text{CdCl}_2/\text{CdCl}_4^{2-}$  couple is identical to that in a basic melt. The electrochemical window of  $\text{Cd(II)}$  buffered melts is 3.5V. Deposition of  $\text{Cd}$  was observed at ca -1V.

## C. General Electrochemistry

Work in this area involves studies related to the application of micron diameter electrodes to study electrochemical processes in molten salts.

## 1. Studies in LiCl-KCl

This work is included for completeness, since it is related to this project. However, funding for this work was from SDIO/IST, and managed through the Office of Naval Research. A manuscript was published in the Journal of the Electrochemical Society. See Ref. 99 in Appendix A.

### ABSTRACT

Tungsten microelectrodes (diam = 25  $\mu\text{m}$ ) have been used to study the deposition and stripping behavior of  $\text{Li/Li}^+$  and  $\text{Bi/Bi}^{3+}$  in the LiCl:KCl eutectic at 400°C. The Li deposition current can be simulated assuming the growth of a single hemisphere of liquid metal on the microelectrode. High stripping current densities were observed and quantitated using standard electrochemical equipment. An inverted microscope assembly was employed for *in situ* observations of the  $\text{Li/Li}^+$  deposition and stripping processes at the microelectrode. A precipitate appears to form in the melt surrounding the electrode during Li deposition.

## 2. Boundary Renewal in Pulse Voltammetry

Although supported by the National Science Foundation, this work is relevant to our objectives in this area and is included for completeness. A manuscript entitled "Renewal of Boundary Conditions in Pulse Voltammetry at Microdisk Electrodes for Non-Reversible Systems" was published in the Journal of Electroanalytical and Interfacial Chemistry". See Ref. 109 in Appendix A.

### ABSTRACT

Normal and reverse pulse (NP and RP) voltammetry of dopamine and epinephrine at stationary microdisk electrodes have been studied to assess the time parameters required for renewal of boundary conditions. For quasi-reversible systems, the proper choice of the initial potential in an NP experiment results in boundary renewal as for reversible systems. Experimental effects attributed to depletion were found to be close to those predicted from an equation relating the errors in the NP limiting current to ratios of pulse width to waiting time. Depletion effects observed in RP experiments were similar to those for NP experiments at the same ratio of time parameters. For irreversible systems and/or systems with follow-up chemical reactions, longer waiting times are needed for boundary renewal. Even for such systems, an adequate renewal of the surface boundary condition is assured at waiting times which are characterized by the dimensionless parameters appropriate for the experiment.

### 3. Short Time Pulse Voltammetry

Efforts were made to develop a technique for very fast, microsecond, pulse voltammetry and apply the technique to the molten salt system. A manuscript "Short Time Pulse Voltammetry at Very Small Electrodes in Ambient Temperature Chloroaluminate Ionic Liquids" was published in the Journal of the Electrochemical Society. See Ref. 115, Appendix A.

#### ABSTRACT

Pulse voltammetry experiments with pulse times as short as 10 $\mu$ s were utilized for the study of electrochemical processes in ambient temperature chloroaluminate ionic liquids. The electrochemical processes studied were the first and second oxidation of anthracene, the kinetics of the Fe(III)/Fe(II) chloro-complexes heterogeneous electron transfer, and the electrochemical/chemical mechanism of Ti(IV) oxychlorocomplex reduction. The working electrode was a Pt disk whose diameter was 26  $\mu$ m. Discrimination against capacitive currents was very good and voltammograms were obtained within seconds thus allowing for averaging of multiple scans.

### 4. Study of Titanium Electrochemistry

A continuation of prior work on Ti in the ambient temperature ionic liquids was carried out in collaboration with the Frank J. Seiler Research Laboratory. A manuscript based on this work was published in Inorganic Chemistry. See Ref. 104 in Appendix A.

#### ABSTRACT

The electrochemistry of titanium (IV) has been examined in acidic (AlCl<sub>3</sub> rich) compositions of the ambient temperature molten salt, AlCl<sub>3</sub> and 1-methyl-3-ethyl-imidazolium chloride (ImCl). Titanium is reduced to Ti(III) and Ti(II) in two one-electron steps, both of which exhibit slow electron-transfer kinetics. The <sup>49</sup>Ti NMR spectra for TiCl<sub>4</sub> and AlCl<sub>3</sub> rich melts exhibit a resonance at ~4ppm (<sup>49</sup>Ti = 0 ppm for neat TiCl<sub>4</sub>). In basic (chloride rich) melts, the <sup>49</sup>Ti resonance for TiCl<sub>6</sub><sup>2-</sup> is found at ~237 ppm. In acidic melts, Ti(IV) is alkylated upon addition of Me<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> and is slowly reduced to Ti(III). Combination of TiCl<sub>4</sub> and Me<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> in an acidic melt is demonstrated to be a catalytic system for ethylene polymerization.

### 5. Reduction of Dioxygen

Although we had never seen the reduction of dioxygen in these molten salts, Prof. Charles Hussey, at the University of Mississippi, had obtained a reduction wave and reported this to us. We carried out collaborative work on

this, with great difficulty and not a great deal of success, but a Note was published in Inorganic Chemistry. See Ref. 108 in Appendix A.

### ABSTRACT

The voltammetric behavior of dioxygen was examined in an ambient temperature molten salt composed of  $\text{AlCl}_3$  and 1-methyl-3-ethyl-imidazolium chloride. A single, totally irreversible reduction was found in a basic melt at a freshly cleaned glassy carbon electrode. The electrode quickly passivated and no reduction wave could be observed after several voltammetric scans. No reduction wave could be observed in an acidic melt, suggesting much more rapid passivation of the electrode surface.

#### D. Chemistry and Electrochemistry in Superacid Systems

The addition of proton to an acidic melt results in a superacid. Here we report on studies aimed at understanding the behavior of proton and the acid/base characteristics of the ambient temperature molten salt system.

##### 1. Oxide and Hydroxide Species

A manuscript entitled "Oxide and Hydroxide Species Formed on Addition of Water in Ambient Temperature Chloroaluminate Melts: An  $^{17}\text{O}$  NMR Study" was published in Inorganic Chemistry. See Ref. 103 in Appendix A.

### ABSTRACT

The variation of the intensity of  $^{17}\text{O}$  NMR lines with manipulation of proton concentration and melt composition has been used to model oxy- and hydroxychloroaluminate species in the ambient temperature molten salt system 1-methyl-3-ethylimidazolium chloride/aluminum chloride. It is concluded that the most probably oxychloroaluminate species in acidic melts are  $\text{Al}_3\text{Cl}_9\text{O}^{2-}$  and either  $\text{Al}_3\text{O}_2\text{Cl}_6^-$  or  $\text{Al}_2\text{OCl}_5^-$ , and the most probable hydroxychloroaluminate species are  $\text{Al}_3\text{Cl}_9\text{OH}^-$  and  $\text{Al}_2\text{Cl}_6\text{OH}^-$ , with the latter being favored. In the basic melts, the most probable oxy- and hydroxychloroaluminate species are  $\text{Al}_2\text{OCl}_5^-$  and  $\text{Al}_2\text{Cl}_6\text{OH}^-$ .

##### 2. Donor-Acceptor Properties

An effort to correlate the ambient temperature molten salt systems acidity scale to the classic Gutmann donor-acceptor concept was made. A manuscript on this work was published in Inorganic Chemistry. See Ref. 100 in Appendix A. (This work was in press at the time the previous Final Report was written, but is included here for completeness.)



## ABSTRACT

The donor-acceptor properties of room-temperature chloroaluminate ionic liquids, composed of mixtures of  $\text{AlCl}_3$  with either N-(1-butyl)pyridinium chloride or 1-ethyl-3-methylimidazolium chloride were studied. Gutmann donor and acceptor numbers were determined by using the  $\text{Eu(III)}$  reduction potential and the  $^{31}\text{P}$  chemical shift of triethylphosphine oxide, respectively. Acidic melts are extremely poor donor and strong acceptor media. Basic melts are similar in basicity to DMF. No conclusions concerning the acceptor properties of the basic melt are drawn from this work since the strongly basic probe molecule,  $\text{Et}_3\text{P}=\text{O}$ , is leveled by the solvent. Conditions under which these parameters are potentially useful are outlined.

## 3. Mixed Bronsted Lewis Acid Adducts

Two manuscripts on this topic were published; the first was a Communication, the second a full paper, in the Journal of the American Chemical Society. Only the abstract of the full paper is given below. See Ref's. 101 and 107 in Appendix A.

## ABSTRACT

A mixed Lewis-Bronsted acid ambient temperature chloroaluminate molten salt, in which both the Lewis and Bronsted acidity may be varied, has been investigated making use of a probe solute molecule. The interaction of the proton and molten salt solvent with N,N-dimethylaniline has been investigated making use of electrochemistry and NMR spectroscopy. The ambient temperature chloroaluminate molten salt, composed of 1-ethyl-3-methylimidazolium chloride,  $\text{ImCl}$ , and aluminum chloride, is the underlying Lewis acid substrate, to which a proton source,  $\text{ImHCl}_2$ , is added. DMA is oxidized in both the basic and acidic melts in the absence of proton and forms an  $\text{AlCl}_3$  adduct in an acidic (excess  $\text{AlCl}_3$ ) melt; the potential for oxidation in the acidic melt is considerably more positive than that in the basic melt. Upon addition of proton, the DMA oxidation wave disappears. In a basic melt (excess  $\text{ImCl}$ ), an amperometric titration indicates that DMA reacts quantitatively with protons, added as  $\text{ImHCl}_2$ , to form  $\text{DMAH}^+$ , which is not oxidized in the melt window.  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy show changes in chemical shifts consistent with these observations.  $\text{DMAH}^+$  shows a reduction wave at potentials more negative than that shown by "free" proton reduction in the basic melt; reverse pulse voltammetry from the limiting plateau for this reduction wave shows a  $\text{H}_2$  oxidation wave and reappearance of the DMA oxidation wave. These results indicate that the process corresponds to the reduction of the proton from the  $\text{DMAH}^+$  to yield  $\text{H}_2$  and DMA at the electrode surface. In an acidic melt, DMA forms an  $\text{AlCl}_3$  adduct; on addition of proton, a  $\text{DMAH}^+$  species, which cannot be oxidized in the melt window, is formed. However, the

reaction of the DMA- $\text{AlCl}_3$  adduct in the acidic melt with proton appears to be less quantitative than the reaction of proton with DMA in the basic melt. Again, the  $^{13}\text{C}$  and  $^1\text{H}$  NMR support these observations.

#### 4. Proton Removal

In performing the studies referenced above, it was necessary to develop a procedure for proton removal. A manuscript describing the procedure was published in *Analytical Chemistry*. See Ref. 112 in Appendix A.

#### ABSTRACT

The application of high vacuum effectively removes protons from ambient temperature chloroaluminate ionic liquids, or molten salts, consisting of mixture of 1-ethyl-3-methylimidazolium chloride and aluminum chloride. Electroanalytical and NMR techniques are used to show the efficacy of the proton removal process. In addition, a combination of electroanalytical and NMR measurements suggests that protons, when present in these ionic liquids as Al-O-H entities, are not electrochemically active.

#### E. Miscellaneous

An EPR study of solvation in these ambient temperature molten salts was undertaken and a manuscript published in the *Journal of Physical Chemistry*. See Ref. 113 in Appendix A.

#### ABSTRACT

EPR spectra of 2,2,6,6-tetramethylpiperidine-1-oxyl (tempo) and of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (tempamine) were obtained in ionic liquids composed of 1-ethyl-3-methylimidazolium chloride,  $\text{ImCl}$ , and aluminum chloride and in mineral oil. In basic solutions, those containing a molar excess of  $\text{ImCl}$ , the rotational correlation time of tempamine was ca. 27 times longer than for tempo. This is probably the result of a specific interaction of melt species with the basic  $\text{NH}_2$  moiety of tempamine. The  $^{14}\text{N}$  hyperfine coupling constant of tempo, 20.5 G, is appreciably larger due to adduct formation with  $\text{AlCl}_3$ .

Five articles were also published in two different volumes of the *Electrochemical Society's Proceedings of the Seventh and Eighth International Symposia on Molten Salts*. These are Ref. 116 to 120 in Appendix A.

## II. Work in Press and in Progress

There was a good deal of work in progress at the conclusion of this grant period, mainly involving manuscripts which were in the process of being written. At the time of the move to North Carolina State University in July, 1992, four manuscripts were in press. These were "Electrochemical and Spectroscopic Study of Anthracene in a Mixed Lewis-Bronsted Acid Ambient Temperature Molten Salt System", in press in *Electrochimica Acta*, "Interaction of 9,10-Anthraquinone with Tetrachloroaluminate and Proton in Basic Aluminum Chloride: 1-Ethyl-3-Methylimidazolium Chloride Room Temperature Molten Salts", in press in the *Journal of the Electrochemical Society*, and "Proton Speciation in Ambient Temperature Chloroaluminate Ionic Liquids", in press in *Inorganic Chemistry*, and "Electrochemical Studies of Tris-(acetylacetonato)ruthenium(III) Complex in Ambient Temperature Chloroaluminate Molten Salts", in press in *Inorganic Chemistry*. See Ref's. 121 to 124 in Appendix A.

In addition, several other manuscripts were being prepared for submission. The titles of these, at least tentatively, are: 1) Electrode Processes of ( $\eta^5$ -Cyclopentadienyl)-(1,2-Substituted 1,2 Ethylenedithiolato) Cobalt(III) Complexes in an Ambient Temperature Molten Salt; 2) Short Time Pulse Voltammetric Studies of Fast Heterogeneous Electron Transfer Reactions; 3) Dependence of Electron Transfer Kinetics of the Ferrocene/Ferrocenium Couple on the Viscosity in Ambient Temperature Chloroaluminate Ionic Liquids; 4) NMR Studies of the Proton Equilibrium in Basic Ambient Temperature Chloroaluminate Ionic Liquids. These will be discussed in the Final Report on the following project.

It must be realized that, at the conclusion of this grant period, we were engaged in packing up the laboratory preparing to move!

## III. Interaction with Air Force Laboratories and Personnel

Interactions, via telephone and visits, were held with a number of the personnel at the Seiler Laboratory. A joint effort resulted in a publication. Captain Paul Trulove completed his Ph. D. at the State University of New York and joined the Seiler Research Laboratory in the Fall of 1991.

## IV. Other Activities

In May, 1990, the principal investigator received the Jacob F. Schoellkopf Award of the Western New York Section of the American Chemical Society; the Award was presented at a banquet.

The principal investigator was the recipient of the 1991 American Chemical Society Division of Analytical Chemistry Award in Electrochemistry. The Award was presented at a Symposium at the American Chemical Society meeting in New York in August, 1991.

The principal investigator was also the recipient of the 1992 Max Bredig Award in Molten Salt Chemistry, presented by the Physical Electrochemistry Division of the Electrochemical Society at the Society meeting in St. Louis in May, 1992. The long-time support of AFOSR in supporting work which lead to this award was acknowledged at that meeting, and in this Final Report.

Talks presented at various meetings during the grant period are given in Appendix B.

## V. Personnel

Personnel associated with this activity for any extended time during the grant period are listed below.

### Senior Research Personnel:

Dr. Jinsong Tang  
Dr. Michael Carter  
Dr. William Ryan  
Dr. John O'Dea  
Dr. Shihua Song  
Dr. Dow Maharajh  
\*Dr. Robert Allendoerfer

### Junior Research Personnel:

Mr. Marc A.-M. Noël<sup>+</sup>  
Captain Paul Trulove <sup>\*,+</sup>

### Secretarial Personnel

Ms. Rosanne Leggio

\*Not paid on grant funds

<sup>+</sup>Ph.D. received during grant period

## APPENDIX A

Publications—Grant Related Activity - since AFOSR support initiated.

AFOSR-71-1955; 1 Jan. 1971 - 28 Feb. 1975

1. Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters", *Electrochimica Acta*, 16, 525 (1971).
2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry", Vol. II, "Application of Computers to Chemical Instrumentation", Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
3. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Solvent Equilibria in  $\text{AlCl}_3\text{-NaCl}$  Melts", *J. Electrochem. Soc.*, 120(2), 223 (1973).
4. H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrode Reactions in Fused  $\text{AlCl}_3$  Containing Solvents", *J. Electroanal. Chem.*, 38, 476 (1972).
5. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in  $\text{AlCl}_3\text{-NaCl}$  Melts", *J. Electroanal. Chem.*, 121, 212 (1974).
6. H. Lloyd Jones and R. A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused  $\text{AlCl}_3$  :II.", *J. Electroanal. Chem.*, 49, 281 (1974).
7. R. J. Gale and R. A. Osteryoung, "Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten  $\text{NaCl-AlCl}_3$  Solvents", *J. Electrochem. Soc.*, 121, 983 (1974).
8. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate", *J. Org. Chem.*, 39, 2416 (1974).
9. H. Lloyd Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroaluminate Solvents", *Advances in Molten Salt Chemistry*, Vol. 3, Edited by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Publishing (1975).

10. R. J. Gale and R. A. Osteryoung, "Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvent", *Inorg. Chem.*, 14, 1232 (1975).
11. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, "An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt", *J. Am. Chem. Soc.*, 97, 3264 (1975).
12. D.E. Bartak and R. A. Osteryoung, "The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate", *J. Electrochem. Soc.*, 122, 600 (1975).
13. J. Phillips, R. J. Gale, R. G. Wier and R. A. Osteryoung, "Glassy Carbon Rotating Ring-Disc Electrodes for Molten Salt Studies", *Anal. Chem.*, 48, 1266 (1976).
14. D. E. Bartak and R. A. Osteryoung, "The Redox Behavior of Tetrachloro-p-Benzoquinone-Tetrachlorohydroquinone Systems in Molten Aluminum Chloride-Sodium Chloride Solvents", *J. Electroanal. Chem.*, 74, 69 (1976).

AFOSR 75-2776; 1 March 1975 - 31 May 1976

15. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylations in a Room Temperature Molten Salt Media", *J. Am. Chem. Soc.*, 98, 5377 (1976).
16. K. A. Paulsen and R. A. Osteryoung, "Electrochemical Studies on Sulfur and Sulfides in  $\text{AlCl}_3$ -NaCl Melts", *J. Am. Chem. Soc.*, 98, 6866 (1976).
17. R. A. Osteryoung, "Chemistry and Electrochemistry in Aluminum Chloride Molten Salt Systems", *Proceedings of the Symposium on Molten Salts*, edited by J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, pp. 240-253, The Electrochemical Society, Pennington, NJ (1976).

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## In Press:

121. Richard Carlin, Paul Trulove and Robert A. Osteryoung, "Electrochemical and Spectroscopic Study of Anthracene in a Mixed Lewis-Bronsted Acid Ambient Temperature Molten Salt System", *Electrochim. Acta*, in press.
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## Appendix B:

Presentations at Meetings Related to Grant Activities  
AFOSR 90-0099; 1 December, 1989 - 30 June, 1992

## Invited Presentations

256. R. T. Carlin, R. A. Osteryoung, J. Wilkes and J. Rovang, "Studies of Titanium(IV) Chloride in a Strongly Lewis Acidic Molten Salt: Electrochemistry, Ti NMR and Electronic Spectroscopy", Symposium on Mechanistic Aspects of Inorganic and Organometallic Chemistry, The Electrochemical Society, Spring Meeting, Montreal, May 6-11, 1990.
257. Soo-Gil Park, Paul Trulove, R. T. Carlin and R. A. Osteryoung, "Protons in Ambient Temperature Chloroaluminate Molten Salts: Electrochemical and NMR Studies of their Interaction with Dimethylaniline and Anthraquinone", Keynote Lecture, Seventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, Montreal, May 6-11, 1990.
258. Paul Trulove, R. T. Carlin and R. A. Osteryoung, "Interaction of Protons with Solutes in Ambient Temperature Chloroaluminate Molten Salts: Electrochemistry and NMR Spectroscopy of Protonated and Unprotonated Anthracene", Seventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, Montreal, May 6-11, 1990.
259. Richard T. Carlin and Robert A. Osteryoung, "A Microelectrode's View of a Chloroaluminate Ambient-Temperature Molten Salt", ANACHEM Award Symposium on Modern Analytical Voltammetry, Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Cleveland, October 7-12, 1990.
260. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft", Colloquium Speaker, Department of Chemistry, University of Tennessee, Knoxville, TN, Feb. 28, 1991.
261. Robert A. Osteryoung, "Pulse Voltammetry - Techniques and Applications", Colloquium Speaker, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, March 1, 1991.
262. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft", Colloquium Speaker, Division of Chemistry, Alfred University, Alfred, New York, April 8, 1991.
263. Marc A. M. Noël, John J. O'Dea and R. A. Osteryoung, "Short Time Pulse Voltammetry in Ambient Temperature Chloroaluminate Ionic Liquids", Symposium on Electrode Processes, Spring Meeting, The Electrochemical Society, Washington, May 5-10, 1991.

264. Robert A. Osteryoung, "Pulse Voltammetry: Saturday's Child", American Chemical Society Division of Analytical Chemistry Electrochemistry Award Address, American Chemical Society Fall Meeting, New York, August, 1991.
265. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft", Seminar, University of Arizona, October 11, 1991.
266. Janet G. Osteryoung, Robert A. Osteryoung and John J. O'Dea, "Pulse Voltammetry '92: Retrospect and Prospect", Symposium "Back to the Future: New Horizons in Electroanalytical Methods and Materials", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March, 1992.
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268. Michael T. Carter and Robert A. Osteryoung, "Electrochemistry of 9,10-Anthraquinone in the Presence of Proton and Tetrachloroaluminate in Ambient Temperature Molten Salts", 8th International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, St. Louis, May, 1992.
269. Paul C. Trulove and Robert A. Osteryoung, "The Nature of Proton in Ambient Temperature Chloroaluminate Molten Salts", 8th International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, St. Louis, May, 1992.
270. Paul C. Trulove and Robert A. Osteryoung, "The Chemistry of Proton in Ambient Temperature Chloroaluminate Molten Salts", 8th International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, St. Louis, May, 1992.
271. Robert A. Osteryoung, "Through the Years and Temperatures: Adventures in Molten Salt Land", Max Bredig Molten Salt Award Address, 8th International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, St. Louis, May, 1992.
272. Robert A. Osteryoung, "Prof. H. A. Laitinen - A Long-ago Student's View", Division of Analytical Chemistry Memorial Symposium Honoring Herbert A. Laitinen, American Chemical Society, Fall Meeting, Washington, D.C., August, 1992.

#### Contributed Presentations

70. Zenon Karpinski, Soo-Gil Park and R. A. Osteryoung, "Reverse Pulse Voltammetric Studies of Reproportionation in Ambient Temperature Molten Salts", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New York, March 4-9, 1990.
71. Marc A.M. Noël and R. A. Osteryoung, "Pulse Voltammetric Determination of the Stoichiometry of Complex Ions in Ambient Temperature Molten Salts", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New York, March 4-9, 1990.
72. Paul C. Trulove, Marc A.M. Noël, and R. A. Osteryoung, "The Nature of Proton in Ambient-Temperature Chloroaluminate Molten Salts", Eighth Annual Chemistry Graduate Student Symposium, SUNY-Buffalo, May 23-24, 1990.
73. Marc A.M. Noël and R. A. Osteryoung, "Preparation of Neutral Ambient Temperature Molten Salts", Eighth Annual Chemistry Graduate Student Symposium, SUNY-Buffalo, May 23-24, 1990.
74. John J. O'Dea, Janet G. Osteryoung and Robert A. Osteryoung, "Analysis of Pulse Voltammograms by the "COOL" Algorithm on a PC", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, March, 1991.
75. Paul C. Trulove and R. A. Osteryoung, "Proton Equilibria in Ambient Temperature Chloroaluminate Molten Salts", Ninth Annual Chemistry Graduate Student Symposium, SUNY-Buffalo, May 22-23, 1991.
76. Marc A-M Noël and R. A. Osteryoung, "Solvation in Ionic Liquids: An EPR Study", Ninth Annual Chemistry Graduate Student Symposium, SUNY-Buffalo, May 22-23, 1991.

## COMPLETED PROJECT SUMMARY

**TITLE:** STUDIES IN LEWIS ACID AND SUPERACID IONIC LIQUIDS

**PRINCIPAL INVESTIGATOR:** Dr. Robert A. Osteryoung  
Department of Chemistry  
State University of New York  
Buffalo, NY 14214

**INCLUSIVE DATES:** 1 December, 1989 - 30 June, 1992

**GRANT NO:** AFOSR 90-0099

**COSTS AND FY SOURCE:** \$120,325 FY 90; \$150,777 FY 91; \$36,491 FY 92

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\*Not paid on grant funds

<sup>+</sup>Ph.D. received during grant period

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\*R. T. Carlin and R. A. Osteryoung, "Deposition Studies of Lithium and Bismuth at Tungsten Microelectrodes in LiCl:KCl Eutectic", J. Electrochem. Soc., 136, 1249-1255 (1989).

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\*\*Work relevant to grant but supported by NSF.

#### **ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS**

The objective of this work was to perform chemical and electrochemical studies in an ionic liquid, a mixture of aluminum chloride and 1-ethyl-3-methylimidazolium chloride. In addition, studies of this system, and solutes therein, on addition of a Bronsted acid were also carried out. Work carried out was in the major areas of: a) studies of modified (polymer coated) electrodes; b) neutral melts; c) general electrochemistry, with emphasis on fast voltammetry at very small electrodes; d) chemistry and electrochemistry in superacid systems.

In the polymer coated electrode area, work was carried out on the behavior of films of polyaniline prepared in both aqueous solutions, and used in the melts, and prepared in the melts, and used in aqueous solutions. Behavior of these filmed electrodes, following transfer from one media to the other, appeared reversible. A study of simultaneous EPR and electrochemistry was also carried out.

Work in neutral melts encompassed a study of the stoichiometry of several inorganic solutes in "near neutral" melts, wherein an amperometric titration of chloride could be utilized to



deduce complex stoichiometry and a study of solutes in a buffered neutral melt, where  $\text{CdCl}_2$  was employed as a buffer.

In the general electrochemical area, under work related to, but not supported by AFOSR, a study at very small electrodes in molten  $\text{KCl-LiCl}$  was carried out. Also in related, but not AFOSR supported work, studies of conditions required to renew the boundary at a very small electrode when the electrode reaction was not reversible, was performed. Work on very short time pulse voltammetry was carried out in the ambient temperature molten salt; pulse times as short as 10 microseconds were employed. The electrochemistry of  $\text{Ti(IV)}$  was examined in an acidic melt, and catalysis of ethylene to polyethylene was observed. Finally, the reduction of oxygen was examined at glassy carbon electrodes in a basic melt; no reduction could be seen in an acidic melt apparently due to rapid electrode passivation.

A good deal of work was carried out on the melts when proton was added deliberately, as  $\text{ImHCl}_2$ , and as an impurity, mainly from water. The oxide and hydroxide species present in the melts due to the presence of water were studied by NMR spectroscopy. Donor acceptor properties of the solvent ambient temperature ionic liquid were obtained. Mixed Bronsted and Lewis acid adducts of dimethylaniline were observed, and the behavior the system examined by electrochemistry and NMR spectroscopy. Finally, a new procedure for the removal of protons was demonstrated.